



Project Summary

Acetonitrile Field Test

Joette L. Steger, Joan T. Bursey, and David Epperson

Abstract

Field experiments were conducted at a hazardous waste incinerator. The ability of a specially-designed sampling train to quantitatively collect acetonitrile was evaluated. Ten quadruple runs were conducted. Each run consisted of four acetonitrile sampling trains sampling simultaneously. The sampling and analytical methods were evaluated using Method 301 (*"Protocol for the Field Validation of Emission Concentrations from Stationary Sources"*) statistical procedures.

The acetonitrile sampling train was based on the Method 0010 train which collects semivolatile compounds on Amberlite XAD-2[®] sorbent. The Method 0010 train was modified by replacing the Amberlite XAD-2[®] with Carboxen[™]-1000. Forty-eight grams of 45/60 mesh Carboxen[™]-1000 were used.

The acetonitrile sampling train was evaluated in the field to demonstrate its ability to determine acetonitrile in the gaseous waste stream from a hazardous waste incinerator. Two of the quadruple trains were dynamically spiked with an aqueous solution of acetonitrile. Method 301 statistical analysis was performed. The mean recovery for the 20 spiked trains was 100%. The relative standard deviation in the measured acetonitrile for the 20 spiked trains and for the 20 unspiked trains was within the Method 301 criteria of <50%. The calculated bias was insignificant; therefore, a bias correction factor was not needed.

This report was submitted in fulfillment of EPA Contract No. 68-D4-0022 by Eastern Research Group under the sponsorship of the United States Environmental Protection Agency. This report covers a period from February 21, 1996 to September 30, 1996, and work was completed as of September 30, 1996.

This Project Summary was developed by the National Exposure Research

Laboratory's Human Exposure and Atmospheric Sciences Division, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

There is a wide interest in developing and evaluating a method for measurement of acetonitrile emissions from stationary sources of air pollution. Acetonitrile is a component of many industrial hazardous waste streams, especially from fiberglass and synthetic fiber manufacturing. Acetonitrile is listed as one of the most difficult compounds to incinerate according to the University of Dayton Research Institute incinerability ranking.¹ Acetonitrile has been suggested as an excellent non-halogenated compound to use as a hazardous constituent spike during Resource Conservation and Recovery Act (RCRA) Subpart-B trial burn tests. Lack of an effective sampling and analysis method has prevented its utilization. Eastern Research Group, under contract to the U.S. Environmental Protection Agency (EPA), has developed and evaluated a method for sampling and analyzing acetonitrile from stationary sources. The results of a field test of that method are provided in this project summary.

Laboratory evaluation of a sorbent based sampling method using the modified Method 0010² train was completed on WA 4 of Contract 68-D4-0022. Final laboratory method evaluation indicated that 48 grams (g) of Carboxen[™]-1000 (the amount that fits in a Method 0010² sorbent module) is sufficient to collect and recover 90 to 100% of the acetonitrile under the conditions tested. Greater than 90% of the acetonitrile can be recovered by eluting the sample from the sorbent. The estimated detection limit for the method is 60 ppbv (100 µg/m³).

A field test of the acetonitrile sampling train developed in the laboratory was con-

ducted under this work assignment (WA 45 of Contract 68-D4-0022). The field test experimental design followed guidance outlined in EPA Method 301,³ "Protocol for the Field Validation of Emission Concentrations from Stationary Sources," 40 Code of Federal Regulations (CFR) Part 63. The field test data were used to determine the method's precision and accuracy.

The field test used a "quad train" approach in which four acetonitrile sampling trains were operated simultaneously to collect flue gas samples. A Method 0010² sampling train, modified by placing CarboxenTM-1000 in the sorbent module, was used to collect gaseous acetonitrile from a hazardous waste incinerator. The acetonitrile was then desorbed from the CarboxenTM-1000 with methylene chloride. The resulting organic extract was analyzed by gas chromatography with flame ionization detection (GC/FID).

Experimental Approach

The purpose of the sampling program was:

- To evaluate the laboratory developed acetonitrile sampling and analytical methods, and
- To determine the performance (precision and accuracy) of the laboratory developed methods under field conditions.

The field test included ten quadruple runs. For each quadruple run, four independent flue gas samples were collected simultaneously from an incinerator emission source. Two of the flue gas streams were dynamically spiked with known concentrations of acetonitrile. The precision of the test method was estimated from the variation in results obtained for pairs of spiked and unspiked samples. Accuracy (bias) was determined from the differences between the spiked and measured quantities of acetonitrile.

Both the sorbent extract and condensate samples collected from each of the trains were analyzed for all of the quad runs to determine whether acetonitrile breaks through the sorbent. The impinger components of the trains were not analyzed and were archived.

For Run 4 (Day 2) and Run 5 (Day 3), five of the seven recovered components were analyzed separately. These five components are:

- The rinse of the front half of the filter housing;
- The 1:1 methylene chloride:methanol extract of the filter;
- The methylene chloride extract of the sorbent;

- The rinses of the back half of the filter housing and condenser; and
- The condensate and condensate rinses.

Probe rinses were collected at the end of each day. The probe rinses from the second and third day were also analyzed, in order to coincide with the detailed analyses performed on Runs 4 and 5 taken on the same days. The analytical results from these six components were examined. Because no acetonitrile was detected in these fractions, the Work Assignment Manager (WAM) decided not to analyze the rinse of the front half of the filter housing, the 1:1 methylene chloride:methanol extract of the filter, the rinses of the back half of the filter housing and condenser for the remaining eight quad trains. For the same reason, the WAM also decided not to analyze the probe rinses from the remaining test days. The analytical results from the sorbent extract and condensate samples were combined for statistical analysis.

Spiking

Two of the four trains making up the quad assembly were spiked during each quad run. Ten complete quad runs resulted in a total of 20 spiked and 20 unspiked trains. Acetonitrile in water was used to spike the trains. Acetonitrile was spiked at a level equivalent to 45 ± 5 ppmv (73 ± 8 milligrams [mg] total) in the flue gas stream. (No acetonitrile was detected in the pre-test site survey samples.)

The spiking procedure for the field validation was identical to that used in the laboratory study for acetonitrile. During each quad run, standard acetonitrile solution was introduced to two of the four trains. The flow rate of the liquid spike into each train was nominally 0.25 to 0.33 mL/min. This spike rate resulted in the introduction of 55 to 91 mg of acetonitrile in each spiked acetonitrile train over a 1-hour sampling period. Approximately 960 L (34 ft³) of sample were collected.

Precision and Accuracy Assessment

This test program was designed to assess precision and accuracy. Precision is defined as the estimate of variability in the data obtained from the entire measurement system (sampling and analysis). At least two (paired) sampling trains are needed to establish precision. Accuracy (bias) is defined as any systematic positive or negative difference between the measured value and the true value. Percent recovery is defined as any gain or loss of a given compound compared to a known spiked value.

Ten quad runs (40 sample trains) were scheduled during the testing program. All 40 independent trains were completed and accepted during the test period. This completion rate exceeded the minimum requirement of at least six quad runs (24 independent trains) for statistical analysis by Method 301.³ This number of runs provided a sample population large enough to produce credible data quality assessments as described later in this section.

The latest version of the "Protocol for the Field Validation of Emission Concentrations from Stationary Sources" (EPA Method 301)³ describes the data analysis method necessary to evaluate both the bias and the precision of emission concentration data from stationary sources. Method 301³ was used for the statistical evaluation of the test data for this field evaluation.

Additional assessment of the precision and accuracy using criteria from the *Quality Assurance/Quality Control (QA/QC) Procedures for Hazardous Waste Incineration Handbook* (EPA/625/6-89/023, January 1990)⁴ was also performed using the criteria for SW 846 Method 0010² ($\pm 50\%$ accuracy and 50% precision).

Results and Discussion

Field Sampling

Ten quad train runs were completed at the field test site. The static pressure in the stack was positive, and remained constant at approximately 6.35 mm (0.25 inches) of water during all test runs. The average sample volume collected was 0.959 ± 0.041 dry standard cubic meters (33.9 ± 1.5 dry standard cubic feet). The sampling time was 60 minutes. Moisture values ranged from 15 to 28% by volume. Moisture values were low (15%) for one run because the process was interrupted during the run. The process interruption did not affect the test data. The source did not contain acetonitrile so acetonitrile levels in the unspiked trains were not reduced.

The stack temperature and velocity for each run were measured using a single thermocouple and S-Type pitot tube on the sampling probe assembly. Individual stack gas temperature and pitot tube differential pressure measurements were taken every 10 minutes for each of the four trains at the time the other stack sampling data (gas meter reading, probe temperature, etc.) were recorded. This measurement scheme resulted in some slightly different temperature and velocity data for individual trains for the same run, even though measurements were made with a common probe. These temperature and differential pressure measurement dif-

ferences did not affect the test data because the sample for all four trains was collected from the same point, the volumes collected were recorded, and the data were corrected for the slight differences in sample volume.

The percent isokinetic determination was slightly outside of the 90 to 110% criteria for four trains. These excursions outside the isokinetic criteria did not affect the test data because no acetonitrile was present in the source. The spiking system was operated to inject approximately equal quantities of spiking solution into the two spiked trains during each sampling run. The actual amounts spiked varied from train to train because the syringe pumps did not always deliver exactly the same amount of spiking solution. Spiked quantities were determined by weighing the spiking syringes before and after each test run. The density of the spike solution was assumed to be 1 g/mL. An average of 72.7 ± 7.7 mg of acetonitrile was spiked into the trains.

Analysis

The samples were collected in seven fractions: 1) the probe rinse, the rinse of the front half of the filter housing, the filter, the rinse of the back half of the filter and the condenser rinse, the sorbent, the condensate, and the impinger contents. The probe rinse was collected at the end of each day. The other fractions were collected for each train. Runs 4 and 5 had two sorbent fractions. All of the fractions for Runs 4 and 5, except for the impinger fraction, were analyzed. Runs 1 through 3 and Runs 6 through 10, had one sorbent fraction. Only the sorbent and condensate fractions were analyzed for these runs.

Sorbent Results

All 40 first sorbents from all 10 runs and eight second sorbents from Runs 4 and 5 were analyzed. All of the acetonitrile values reported for the sorbents from the unspiked trains were extrapolated beyond the lowest point of the calibration curve and are estimated values only.

For the spiked trains, the first sorbent in the train collected from 68 to 114% of the spiked acetonitrile. These percentages equate to 47 to 104 mg. Thus, the capacity of the sorbent appears to be at least 104 mg of acetonitrile, 1.04 m^3 , and 303.3 g of water. Method performance may decrease when greater than 104 mg of acetonitrile is collected, or when more than 1.04 m^3 of air is sampled, or more than 303.3 g of water is condensed from the source.

Condensate Analysis

All 40 condensates from all 10 runs were analyzed. Acetonitrile was detected

only in the condensates of the spiked single sorbent trains. No acetonitrile was detected in the condensate from Run 6. Run 6 contained less moisture because the process was interrupted during the run.

For the other 14 spiked single sorbent trains, the condensate in the train collected from <1 to almost 11 mg of acetonitrile. An average of 4 mg of acetonitrile was detected in these condensates. The relative standard deviation was 64%. The high relative standard deviation indicates that there is much variability in the amount of acetonitrile collected in the condensate.

Acetonitrile Recovery

The percentage of acetonitrile recovered in all of the analyzed components of each spiked sampling train ranged from 74 to 119% for the 20 spiked trains. The average recovery was 100%. The relative standard deviation was 13%.

Acetonitrile Breakthrough

The second sorbent module in Runs 4 and 5 were analyzed. Therefore, breakthrough of acetonitrile into the second sorbent could be examined. Any amount of compound detected in the second sorbent was classified as having broken through the first sorbent module.

For the four spiked double sorbent module trains, breakthrough ranged from 2 to 8%. The average breakthrough was 4%. The relative standard deviation was 90%. Three of the trains exhibited 2% breakthrough. One train exhibited 8% breakthrough. Thus, breakthrough of acetonitrile was inconsistent. No reason was identified to explain why breakthrough was higher in the one train.

The condensate fraction was analyzed for Runs 1 through 3 and Runs 6 through 10. Therefore, breakthrough of acetonitrile into the condensate could be estimated. Acetonitrile is not quantitatively collected in water. Thus, some of the acetonitrile that broke through the sorbent may not have been collected. Therefore, breakthrough calculations for the single sorbent modules may be biased low. Any amount of acetonitrile detected in the condensate was classified as having broken through the sorbent module.

No acetonitrile was detected in the condensate for the unspiked single sorbent module trains. Thus, no breakthrough analysis was possible using these samples. For the 16 spiked double sorbent module trains, breakthrough ranged from 0 to 11%. The average breakthrough was 5%. The relative standard deviation was 73%.

Two of the trains exhibited 0% breakthrough. These were the two spiked trains

collected when the process went down. Thus, less moisture was collected during this run than during the other runs. The amount of moisture in the source may contribute to the amount of acetonitrile that breaks through the sorbent.

One train exhibited 11% breakthrough. Calculated breakthrough for all of the other trains was less than 10%. Again, breakthrough of acetonitrile was inconsistent. No explanation of why breakthrough was higher in some trains was identified. Breakthrough was <10% for 95% of the spiked trains. For 50% of the spiked trains, breakthrough was <5%. Use of two sorbent modules in series may be necessary when sampling sources containing >15% moisture.

Statistical Analysis

Method validation statistics were generated according to EPA Method 301³ guidelines. Data for all analyzed fractions from all ten runs were used. Before statistical analysis, all compound quantities from the analytical reports were normalized using the gas volume sampled by each train. Normalization of the data was required because each train collected slightly different sample volumes.

Results for the statistical analysis for acetonitrile were RSDs of 13% for the 20 spiked samples and 17% for the 20 unspiked samples and a bias of 0.07 mg. The bias was insignificant so no correction factor was required. Using the criteria of 50% maximum for the RSD and 1.000 ± 0.300 for the bias correction factor, the method validation test was successful for acetonitrile.

The acetonitrile train also meets the criteria from the *Quality Assurance/Quality Control (QA/QC) Procedures for Hazardous Waste Incineration Handbook* (EPA/625/6-89/023, January 1990)⁴ for SW 846 Method 0010.² The average recovery of 100% is within the QA Handbook⁴ criteria of $\pm 50\%$ accuracy. The relative standard deviation for the spiked trains of 13% is within the QA Handbook⁴ criteria of 50% precision.

Discussion

Three statistical comparisons of the data were made. Total acetonitrile recovered in the train was compared to acetonitrile recovered in the first sorbent module. Total acetonitrile recovered was also compared to acetonitrile breakthrough. Finally, acetonitrile recovered in the first sorbent module was compared to acetonitrile breakthrough. A >90% correlation existed between the total recovery and the amount recovered from the first sorbent module. This correlation indicates that any action

that will increase the retention on and recovery from the first sorbent module will improve the performance of the train.

No correlation was found between the total acetonitrile recovered and the amount of acetonitrile that broke through the first sorbent module. Also, no correlation was found between the acetonitrile recovered on the first sorbent module and the amount that broke through. As expected, in general, the recovery on the first sorbent module increased as the breakthrough decreased.

The effect of gas volume sampled and moisture collected on the total acetonitrile recovery, the recovery of acetonitrile in the first sorbent, and the acetonitrile breakthrough was also investigated. No correlation was found between the volume of gas sampled and the total acetonitrile recovery, the recovery of acetonitrile in the first sorbent or the acetonitrile breakthrough. No correlation was found between the moisture collected and the total acetonitrile recovery or the recovery of acetonitrile in the first sorbent.

A slight correlation (33%) was found between the moisture collected and the percent acetonitrile that broke through the first sorbent module. As the moisture collected increased, the breakthrough increased. This slight correlation may indicate that the performance of the train may be dependent on the amount of moisture present in the source. Additional performance studies of the sampling train should be conducted to determine if a limit on the amount of moisture which can be collected needs to be added to the method.

Carboxen™-1000 should also be a suitable sorbent for collecting other polar, water soluble compounds such as alcohols, ketones, and ethers. Additional performance studies should be conducted to expand the acetonitrile method to other compounds listed in the Clean Air Act, such as methyl ethyl ketone and methyl isobutyl ketone.

Conclusions and Recommendations

The work completed on WA 45 used a modified Method 0010² train at a hazardous waste incinerator to collect and measure acetonitrile. The Method 0010² train was modified by using 48 g of Carboxen™-1000 in place of the Amberlite® XAD-2 sorbent. The following conclusions are based on the results of this work:

- The acetonitrile train, consisting of a Method 0010² train with 48 g of Carboxen™-1000 in the sorbent module, successfully samples and collects

acetonitrile from stationary gaseous emission sources.

- The bias calculated for acetonitrile using Method 301³ statistical procedures was insignificant. Thus, no bias correction factor is needed.
- The relative standard deviations were 13% for spiked trains and 17% for unspiked trains. These standard deviations are within the Method 301³ criteria of < 50%.
- The mean recovery of 100% and relative standard deviation of 13% for the spiked trains is within the EPA's Quality Assurance Handbook⁴ requirements of 50 to 150% recovery and 50% relative standard deviation.
- Greater than 90% of the recovered acetonitrile was collected on the Carboxen™-1000. Essentially no acetonitrile was collected in the probe rinses, in the rinse of the front half of the filter holder, or on the filters.
- For the four spiked trains containing dual sorbent modules, less than 2% of the acetonitrile broke through to the second module for three of the trains and less than 8% broke through in the fourth train.
- For the 16 spiked trains containing single sorbent modules, less than 5% of the acetonitrile broke through to the condensate for eight of the trains and less than 9% broke through for 15 trains.

The following recommendations are based on the results of this study:

- Evaluate the acetonitrile sampling train for other polar, water soluble compounds such as methyl ethyl ketone, methyl isobutyl ketone, acetone, and quinone.
- Use two sorbent modules in series when sampling sources containing >15% moisture.
- Investigate improved or alternate procedures for desorbing the Carboxen™-1000 to recover the acetonitrile. Possible alternate procedures include using high-pressure, low-temperature extraction techniques.
- Develop and test procedures for recovering and reactivating used Carboxen™-1000.
- Evaluate the acetonitrile sampling train at a second field site at a source other than a hazardous waste incinerator. The evaluation should include,

in addition to acetonitrile, other polar, water soluble compounds such as methyl ethyl ketone and methyl isobutyl ketone.

Acknowledgments

Under EPA Contract No. 68-D4-0022 Eastern Research Group prepared this report with the supervision and guidance of Mr. Robert Fuerst, EPA Work Assignment Manager, in the National Exposure Research Laboratory, Air Measurements Research Division, Methods Branch, Research Triangle Park, North Carolina. The Eastern Research Group Project Manager was Joan T. Bursey, and the Principal Investigator was Joette L. Steger. We wish to acknowledge the contributions of the following individuals to the success of this program: Amy Bederka, Jenia Doerle, Danny Harrison, Jim Howes, Linh Nguyen, and Mark Owens.

References

1. *Environmental Science and Technology*, 24, pp 316-328, 1990.
2. *EPA Methods 0010, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods*. S-W-846, Third Edition, September 1988, Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, DC 20460.
3. U.S. Environmental Protection Agency. *Method 301, Protocol for the Field Evaluation of Emission Concentrations from Stationary Sources*. Code of Federal Regulations, Title 40, Part 63. Washington, DC. Office of the Federal Register. July 1, 1987.
4. U.S. Environmental Protection Agency. *Quality Assurance/Quality Control (QA/QC) Procedures for Hazardous Waste Incineration Handbook*. EPA/625/6-89/023, Center for Environmental Research Information, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH 45268. January 1990.

Disclaimer

The information in this document has been funded wholly by the United States Environmental Protection Agency under EPA Contract Number 68-D4-0022 to Eastern Research Group. It has been subjected to Agency review and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Joette L. Steger, Joan T. Bursey, and David Epperson are with Eastern Research Group, Inc., Morrisville, NC 27560.

Robert G. Fuerst is the EPA Project Officer (see below).

The complete report, entitled "Acetonitrile Field Test," (Order No. PB98-133143;

Cost: \$49.00, subject to change) will be available only from:

National Technical Information Service

5285 Port Royal Road

Springfield, VA 22161

Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

Human Exposure and Atmospheric Sciences Division

National Exposure Research Laboratory

U.S. Environmental Protection Agency

Cincinnati, OH 45268

United States
Environmental Protection Agency
Center for Environmental Research Information
Cincinnati, OH 45268

Official Business
Penalty for Private Use \$300

EPA/600/SR-97/140

BULK RATE
POSTAGE & FEES PAID
EPA
PERMIT No. G-35